**Laboratory Name:** Pacific Northwest National Laboratory
**B&R Code:** KC 020102

**FWP and/or subtask Title under FWP:**
Defects and Defect Processes in Ceramics

**FWP Number:** 18048

**Program Scope:**
Research integrates experimental and computational approaches to develop fundamental understanding and predictive models of defect properties and interactions in ceramics. Ion channeling, electron microscopy, and optical and X-ray spectroscopies are used to characterize defect properties, irradiation damage accumulation, phase transformations, and evolution of nanostructures. Ab initio, molecular dynamics and kinetic Monte Carlo methods are used to probe defect energetics, migration processes, defect accumulation, and nanostructure evolution.

**Major Program Achievements (over duration of support):**
Contributed to understanding defect properties and irradiation damage in SiC, GaN, $ZrSiO_4$, $SrTiO_3$, and $A_2B_2O_7$ pyrochlores. Discovered electron-beam induced epitaxial recrystallization in $SrTiO_3$. Developed interatomic potentials for SiC, C, GaN, $ZrSiO_4$ and computational models of epitaxial recrystallization in SiC and of melting and mechanical properties in GaN nanotubes. Discovered process for Cd nanowire formation. Developed new model for irradiation-induced disorder accumulation. Determined electronic stopping power in SiC and binary oxides over continuous energy ranges for numerous ions, and identified deficiencies in current electronic stopping models.

**Program impact:**
Provided globally-adopted scientific understanding, models, displacement energies, and interaction potentials for defects and irradiation effects in ceramics. Provided predictive model applicable to ion-irradiation effects and long-term storage of actinide waste forms. Improved simulation methods for radiation effects in ionic materials. (FY04-06: 88 peer-reviewed journal articles; 2 peer-reviewed book chapters; 7 peer-reviewed conference papers; 3 edited conference proceedings, 33 invited presentations)

**Interactions:**
Theory and computer simulations – L.R. Corrales (Univ. Arizona); C. Meis, A. Chartier, J.-P. Crocombette (CEA-Saclay, France); M. Posselt (Research Center Rossendorf, Germany); A. Cormack (Alfred Univ.); J. Du (Univ. Virginia); E. Bringa (LLNL); Z. Wang, X. Zu (Univ. of Electronic Science & Technology of China)
Experimental Studies – R.C. Ewing, L.M. Wang, J. Lian (Univ. Michigan); L.A. Boatner (ORNL); H.J. Whitlow (Univ. Jyväskylä, Finland); A. Hallén (Royal Inst. of Technology, Sweden); G. Possnert (Uppsala Univ., Sweden); M. Ishimaru (Osaka Univ., Japan); M. Higuchi (Hokkaido Univ., Japan); J.-M. Constantini (CEA-Saclay, France)

**Recognitions, Honors and Awards (at least in some part attributable to support under this program):**
W.J. Weber: *Fellow*, Amer. Assoc. for the Advancement of Science (2006); PNNL 2005 *Chester L. Cooper Mentor of the Year Award*; Chair, International Conferences on *Alternative Nuclear Waste Forms* (2004), *Radiation Effects in Insulators* (2005), *Computer Simulation of Radiation Effects in Solids* (2006), and MRS Symp. on *Growth, Modification, & Analysis by Ion Beams at the Nanoscale* (2005); Member, International Committees for *Radiation Effects in Insulators* and for *Computer Simulations of Radiation Effects in Solids*; Principal Editor, *J. Materials Research*; Member, Editorial Board for *Nucl. Instrum. & Methods in Physics Research, Section B*.
R. Devanathan: Chair, MS&T-2006 Symp. *Radiation Effects in Materials* and MRS 2006 Symp. *Multiscale Modeling of Materials*; Invited National Academy of Engineering 2005 *Frontiers of Engineering* Symposium.
Y. Zhang: 2005 *Presidential Early Career Award for Scientists and Engineers*; 2005 DOE *Office of Science Early Career Scientist and Engineer Award*; Chair, MS&T-2006 Symp. *Ion Beam Modification and Synthesis in Solids*.

**Personnel Commitments for FY2006 to Nearest +/- 10%:**
W.J. Weber (30%), R. Devanathan (40%), Y. Zhang (10%), F. Gao (40%), W. Jiang (90%), H.L. Heinisch (10%), I.-T. Bae (post doc, 60%), Z. Rong (post doc, 60%), J. Du (post doc, 40%)

**Authorized Budget (BA) for FY04, FY05, FY06:**
**FY04 BA $**859k **FY05 BA $**825k **FY06 BA $**959k

**Laboratory Name:** Pacific Northwest National Laboratory
**B&R Code:** KC020105

**FWP and/or subtask Title under FWP:**
Physics and Chemistry of Ceramic Surfaces

**FWP Number:** 10122

**Program Scope:**
Carefully controlled epitaxial growth of pure and doped metal oxides to gain a fundamental understanding of optical, electronic, magnetic and surface chemical properties comprises the central theme of this project. We employ state-of-the-art plasma assisted molecular beam epitaxy, metal organic chemical vapor deposition, pulsed laser deposition, and reactive ballistic deposition to prepare model oxide films in which dopants and high surface area morphologies can be introduced in a controlled fashion. Of particular interest are dopant spin interactions with shallow donor and acceptor states in oxide semiconductors, along with surface uptake and reactivity of highly porous crystalline oxides.

**Major Program Achievements (over duration of support):**
(1) Development of oxygen-plasma-assisted and ozone-assisted molecular beam epitaxy as flexible tools for the preparation of a variety of complex metal oxides. (2) Growth of exceptionally well-defined epitaxial films of magnetically doped transition metal oxide semiconductors and the resulting fundamental understanding that are critical to the nascent field of semiconductor spintronics (3) The discovery of very high polaron-driven p-type conductivity in certain magnetic nickel/cobalt spinel oxides that is promoted by resident disorder within the cation lattice. (4) Pioneering development of reactive ballistic deposition methods for synthesizing ultra-high surface area nanoporous oxide materials. (5) Development of a new method based on cryogenic physisorption to quantify adsorbate binding to and desorption from defect sites on oxide surfaces.

**Program Impact:**
The true nature of defect states and their correlation with film properties in magnetically doped transition metal oxides underpins evolving research in high-$T_c$ dilute magnetic semiconductors for global applications of spintronics materials. For instance, a very strong kinetic correlation between room-temperature ferromagnetism and the presence of shallow donors from interstitial Zn was discovered in Co:ZnO. Additionally, highly conductive p-type transition metal spinel oxides are under investigation as candidate electrode materials for solid oxide fuel cells.

**Interactions:**
Internal - Institute for Interfacial Catalysis, Fundamental Science Directorate, Environmental and Molecular Sciences Laboratory, Materials Science Division, Joint Institute of Nanotechnology – PNNL & UW.
External – U Washington (deposition, characterization, modeling), U Texas Austin (molecule/surface interactions), Yale (magnetotransport), U Florida (electronic structure modeling and spinel oxide conductors); SNL (modeling surface adsorbed water); ANL-APS (XAS and XMCD); LBNL-ALS (XMCD); SSRL (XRD).

**Recognitions, Honors and Awards (at least in some part attributable to support under this program):**
S.A. Chambers: E.W. Muller Award, Fellow AVS, Advisor for NSF MRSECs at Yale and UCSB, Program Chair for the 5th International Workshop on Oxide Surfaces (IWOX-V).
G.J. Exarhos: Editor – VACUUM, AVS Publications Committee Chair, AVS/Surface Engineering Executive Committee, Conference Chair –Optical Materials for High Power Lasers; Fellow (ACerS, AVS, AAAS).
B.D. Kay: DOE/BES Council of Chemical Sciences, BES Materials Sciences Division Committee of Visitors, Fellow (AVS, APS, AAAS); Editorial Board Member (Progress in Surface Science, Journal of Physical Chemistry, (FY 2004-2006) Productivity includes 18 invited presentations, 3 invited review articles, 50 peer-reviewed publications, 3 edited proceedings, and 3 patents.

**Personnel Commitments for FY2006 to Nearest +/- 10%:**
S.A. Chambers (50%), Z. Dohnalek (40%), T.C. Droubay (30%). B.D. Kay (20%), G.J. Exarhos (20%), T. Kaspar (50% postdoc)

**Authorized Budget (BA) for FY04, FY05, FY06:**
FY04 BA $639k FY05 BA $589k FY06 BA $577k

**Laboratory Name:** Pacific Northwest National Laboratory
**B&R Code:** KC020105

**FWP and/or Subtask Title under FWP:**
Molecularly Organized Nanostructural Materials

**FWP Number:** 12152

**Program Scope:**
Nanoporous architectures are prepared using an array of solution templated growth and post growth modification strategies that invoke chemical control of molecular self-assembly at interfaces. Hierarchically ordered structures intrinsic to natural carbohydrates are replicated in ceramics using chemically tailored surfactants or copolymers that induce ordering of preceramic micelles through mediation of inter- and intra-molecular forces. Guidelines for self-assembly are derived from related modeling studies that correlate molecular interaction energy with equilibrium conformation. Materials are characterized with respect to phase composition and homogeneity, and pore structure and pore interconnectivity, by means of non-conventional magnetic resonance measurements and light scattering techniques that are complemented by traditional electron microscopy and x-ray and neutron scattering approaches.

**Major Program Achievements (over duration of support):**
(1) Noble and transition metal nanoparticles form on cellulose nanocrystals by a surface induced reduction reaction; oriented particles align along the molecular axes of the cellulose molecules and reside on the hydroxyl planes.
(2) Mixtures of organic salts and zwitterionic surfactants form ordered nanostructures when melts are cooled in air.
(3) An innovative xenon polarizer has been designed and constructed that facilitates high sensitivity, temperature dependent, continuous flow hyperpolarized (HP) $^{129}$Xe NMR measurements. Bulk pore structure and pore inter-connectivity are characterized in void composite materials by means of temperature-dependent NMR measurements.
(4) Aqueous sugar solution heated to 125 C. in a closed system dehydrates to form homogeneous carbon nano-spheres by a condensation mechanism that invokes hydrophobic phase partitioning from the hydrophilic solution.
(5) Proton NMR identified hydrogen defect states in ZnO nanotubes that are stable to temperatures near 500 C.

**Program Impact:**
- Operando proton and hyperpolarized xenon NMR measurements are key to understanding flow processes and water partitioning in polymer membranes which govern energy conversion efficiency in PEM fuel cells.
- Based upon wood mineralization studies, natural products like cellulose can be manipulated to form ordered, high surface area interfaces that show remarkable catalytic activity or enhanced binding for toxic material sequestration.
- Manipulation of both intra- and inter- molecular forces at interfaces is key to the development of smart materials that respond reversibly to changes in the ambient environment for sensors and actuator applications.
- Computational molecular design yields structure/property relationships that guide synthesis of smart materials.

**Interactions:**
Internal—Fundamental Science Directorate, Environmental and Molecular Sciences Laboratory, Institute for Interfacial Catalysis; Materials Science Division; Environmental Technology Directorate;
External—NRC-Canada (HP Xe NMR determination of porosity), Univ. of Utah (Develop Xe NMR polarizer); Clemson University (solution-derived composite materials), WSU (molecular self-assembly), PSU (CP-MAS Solid State NMR & theoretical simulations); Tennessee Community College (carbon nanosphere formation).

**Recognitions, Honors and Awards (at least in some part attributable to support under this program):**
G.J Exarhos: Society Fellow (ACerS, AVS, AAAS); Editor, VACUUM; AVS Publications Chair; AVS Surface Engineering Division Board; W.D. Samuels: Chair, Local ACS Section; A.D-Q Li: Beckman Young Investigator Award, NIH General Medicine (GM) RO1 Award. (34 publications, 2 book chapters, 17 invited talks, 3 patents).

**Personnel Commitments for FY2006 to Nearest +/- 10%:**
G.J. Exarhos (50%), W.D. Samuels (30%), Y. Shin (60%), L.-Q. Wang (50%), C.F. Windisch, Jr. (30%) A. DeQuan Li (WSU) (30%)

**Authorized Budget (BA) for FY04, FY05, FY2006:**
**FY04 BA $** 760k **FY05 BA $** 732k **FY06 BA $** 693k